Gas-generating material for gas-actuated car safety devices

The purpose of pyrotechnical gas-generating substances used in air-bag assemblies is to fill the fabric pouch of the air bag with a gas quickly, in order to provide a flexible protecting medium between the passenger and the equipment in the car. The pyrotechnical gas-generating substances and the gas formed by them must meet a number of requirements in order to ensure the that the air-bag assembly works and is reliable, and that the environment is not harmed. The same requirements are also placed on the pyrotechnical gas-generating substances used in other gas-actuated safety devices in cars, such as safety-belt tighteners, inflatable neck supports, etc.

Thus, the gas formed in all such car safety devices should not contain any hot solid particles that could burn through the main part of the system and set fire to the gas-filled fabric pouch and injure the passengers or jeopardize the entire operation of the safety device. Sodium azide, the most commonly used pyrotechnical gas-generating substance for this purpose nowadays, does not fully meet this requirement and must therefore be employed with specially reinforced fabric pouches to stop the movement of the solid particles formed in the combustion of sodium azide. The need for this extra reinforcement means that such a safety device is larger and weighs more than strictly needed for its operation.

Furthermore, the environmental requirements placed on the pyrotechnical gas-generating substances used for the purpose in question stipulate that these substances must not form gaseous mixtures that contain poisonous gases in an amount that is harmful to health. The poisonous gases that are mainly relevant in this context because they are formed in the combustion of

the gas-generating substances are nitrous compounds, NO_x and carbon monoxide. If the gas-generating substance contains chlorine, hydrochloric acid is also formed.

Furthermore, the pyrotechnical gas-generating substances used in a gas-actuated car safety device must have a high efficiency, i.e. they should form a large amount of gas per unit weight or volume of the gas-generating substance. However, the efficiency of sodium azide is not particularly high, since it only forms gas in an amount of about 40% of the solid substance. This low efficiency makes it difficult to meet the car manufacturers' requirement of car safety devices with a low weight and a small size when sodium azide is employed as a gas-generating substance.

A further requirement placed on the said pyrotechnical gas-generating substances is that they should all be thermally stable in the sense that they should not be affected much by the high temperatures that can occur in the dashboard in countries with a warm climate. Nitrocellulose is an example of a substance that does not meet this requirement, but which would otherwise be suitable, and in fact it is used nowadays for this purpose, although it limits the service life of the said car safety devices.

In addition to the above requirements, the product used in car safety devices as a pyrotechnical gas-generating substance must also meet several requirements concerning its combustion characteristics if a fully satisfactory operation is to be ensured. Thus, the ideal pyrotechnical gas-generating substance in this connection should have a high rate of burning and one that does not vary much with the pressure or the temperature. Sodium azide is an ideal substance from this point of view, but it has several disadvantages, as mentioned above.

There is another group of substances that generate gases when combusted and which have been tried as gas-generators for car safety devices. This group comprises nitramine-based gunpowder compositions such

as RDX, which are used e.g. in a mixture with cellulose acetyl butyrate. However, the disadvantage of nitramine-based gunpowders is that their rate of burning depends on the pressure to a large extent. If the pressure to too low, the burning is completely extinguished, while if the pressure is too high, the combustion has an explosive course. According to US Patent No. 5,695,216, these disadvantages can be corrected by constructing a powerful container for the gas-forming substance and to equip the container with decompression means. However, even if this functions - and functions well, the construction still requires extra parts and costs more.

The present invention relates to the use of a pyrotechnical gas-generating substance that is completely new in the application under consideration, namely guanidine dinitramide, which has the following chemical formula and which can be easily prepared from guanidine and ammonium dinitramide.

$$\begin{array}{c} \text{N-H} \\ \| \\ H_2N\text{--}C\text{--}NH_3N(NO_2)_2, \end{array} \quad \text{i.e.} \quad CH_6O_4N_6$$

According to the invention, guanidine dinitramide can be advantageously used as a pyrotechnical gas-generating substance in gas-actuated car safety devices such as air bags, safety-belt tighteners, inflatable neck supports, etc. For this purpose, the guanidine dinitramide is employed either in the pure form or in a mixture with other gas-releasing or oxygen-releasing substances, such as for example guanyl urea dinitramide, which can modify the burning rate and the rate of gas evolution of the main substance according to each special requirement.

As mentioned before, the present invention also relates to the mixing of guanidine dinitramide with other substances in order to obtain a mixture whose burning characteristics are optimal for the application in question.

An essential advantage of guanidine dinitramide and of mixtures in which it features as the main component is that these substances contain both oxidizers and a fuel. They are therefore in principle of the type of single-component gunpowder, which does not need any other substance for combustion or has access to atmospheric oxygen.

Pure guanidine dinitramide burns very fast even at a low pressure, and its combustion is not very pressure-dependent, the pressure exponent being about 0.75. At atmospheric pressure, guanidine dinitramide burns faster than nitrocellulose and almost as fast as sodium azide. A significant advantage over sodium azide is, furthermore, that guanidine dinitramide does not form any solid combustion products but is instead fully converted into gases on combustion. This means in turn that, when guanidine dinitramide is used as the gas-generating substance in air-bag assemblies, no extra reinforcement is needed for the gas pouches in order to prevent the substance from burning through them. This fact enables the designers of such car safety devices to reduce the weight and size of the latter without jeopardizing their operation. Moreover, guanidine dinitramide only contains one carbon atom, so that advantageously little carbon monoxide is formed in its combustion. In addition, guanidine dinitramide has an ideal thermal stability, with a melting point in excess of 130°C and a decomposition temperature of over 160°C.

As mentioned before, the rate of burning of guanidine dinitramide, and therefore of course the rate of gas-formation, can be modified by admixing other gas-generating or oxygen-releasing substances to it. A specially suitable additive that can be used in this connection is guanyl urea dinitramide, which has the following chemical formula.

$$H_2N\text{--}\overset{\overset{\displaystyle O}{\|}}{C}\text{--}NH\text{--}\overset{\overset{\displaystyle N\text{-}H}{\|}}{C}\text{--}NH_3N(NO_2)_2, \quad \text{i.e.} \quad C_2H_7O_5N_7$$

Guanyl urea dinitramide is relatively easy to prepare from guanyl urea by reacting it with ammonium dinitramide. Pure guanyl urea dinitramide burns much less fast than guanidine dinitramide, so that it is not all that suitable for use by itself as a gas-generating substance in car safety devices, at least in certain applications. Furthermore, guanyl urea dinitramide contains an additional carbon atom, so that its combustion gases contain too much carbon monoxide when this compound is used as the main gas-generating substance. On the other hand, its combustion is stable even at a low pressure, besides being fairly independent of the pressure and the temperature. Furthermore, guanyl urea dinitramide also burns without forming any solid particles. In addition, it is thermally stable, with a melting point of over 160°C, and its decomposition does not start until 180°C is reached. Its lower rate of burning and its chemical similarity to guanidine dinitramide make it particularly useful as a combustion modifier for regulating the rate of burning of a mixture of these two substances. Mixing these compounds has therefore made it possible to prepare gas-generating materials with a suitable rate of burning for each particular application.

Mixtures of guanidine dinitramide and guanyl urea dinitramide burn with so little smoke that there is no risk of confusing the release of an air-bag assembly with the beginning of a fire in the car, which has sometimes happened before with the previous types of air-bar assemblies, such as those using azides as gas-generating substances.

Both guanidine dinitramide and guanyl urea dinitramide can be pressed into tablets with a good mechanical strength whether they are used singly or in mixtures with each other. This means that both pure guanidine dinitramide and its mixtures with guanyl urea dinitramide are suitable for use in most applications

in the form of pressed tablets. If required, a small amount - preferably not more than 10 wt-% - of a binder may be added to confer an even better mechanical strength on the pressed tablets.

The substances according to the invention have the further advantage that, when they finish their service life as potential gas-generating substances in a car safety device, which hopefully has not seen active use, they can be simply recovered for re-use as gas-generating substances in a similar or a different product.

When preparing new chemicals nowadays, it is essential to bear in mind, for environmental reasons, how they can be recovered and recycled. Yet none of the materials used nowadays as gas-forming substances in car safety devices can be recovered in a simple manner when they have come to the end of their service life without active use. Besides, as these car safety devices are products that preferably should not see active use, it can be expected that the number of unused units of such gas-generators that will have to be collected after the vehicles equipped with them are scrapped will increase at the rate at which these safety devices are installed in new cars.

Sodium azide, which is nowadays used in car safety devices on a large scale, is in fact always employed in a mixture comprising Fe_2O_3 and silicates, and no effective way of re-using these substances is known today. Furthermore, sodium azide is very toxic, which is another reason why there is no other possibility than to destroy it as soon as possible when the car safety device incorporating it has reached the end of its service life. Similarly, nitrocellulose cannot be re-used either, because it is unstable and decomposes in the course of time. The only practical method of destroying nitrocellulose collected from scrapped products is therefore exactly the same as in the case of sodium azide, i.e. incineration.

By contrast, guanidine dinitramide and guanyl urea dinitramide are uniform and stable products that can furthermore be easily recrystallized. If, despite everything, they undergo decomposition to some extent, they can still be recycled after recrystallization. The fact is that this process removes any decomposition products, and so the recrystallized compound is entirely comparable with the newly produced one. A further advantage is that these two compounds can be recrystallized from water without the use of solvents. This possibility of recovering and recycling the gas-generating substances from scrapped car safety devices of the kind considered here has of course significant environmental benefits in comparison with the currently customary azides and nitrocellulose gunpowders, which must always be destroyed by incineration.

Guanidine dinitramide itself is moderately soluble in water at room temperature and is not hygroscopic, whereas guanyl urea dinitramide is fairly insoluble in cold water but moderately soluble in warm water. Both compounds can therefore be recrystallized from water at a low temperature. This is a particularly simple and cheap process, which should make it possible to recover and re-use the gas-generating substances from scrapped but non-deployed air-bag assemblies and similar other pyrotechnically actuated car safety devices.

The various aspects of the invention are specified in the claims, and the attached diagram shows how the rate of burning varies with the combustion pressure in the case of various mixtures of the two compounds in question.

This diagram was constructed on the basis of experimental values obtained as follows. In the case of each mixture, the same amount of sample in the form of pressed tablets was combusted in a hermetically sealed combustion bomb, together with a standard amount of auxiliary gunpowder used as an aid and a pressure-raising additive. The pressure inside the combustion bomb was measured with a manometer, and the rate of

burning was determined from the curves obtained for the change in pressure. The experimental values obtained were used to construct the curves shown in the diagram.

The letters A and B in this diagram refer to guanyl urea dinitramide and guanidine dinitramide, respectively, and the amounts of both are given in the diagram.